

February 10, 1887.

Professor STOKES, D.C.L., President, in the Chair.

The Presents received were laid on the table, and thanks ordered for them.

The following Papers were read :—

- I. "Contributions to the Metallurgy of Bismuth." By EDWARD MATTHEY, F.S.A., F.C.S., Assoc. Roy. Sch. Mines. Communicated by JOHN PERCY, M.D., F.R.S., Pres. Iron and Steel Inst. Received August 18, 1886.

§ 1. *Bismuth: its Separation from Gold, and its Refining Action upon same during the Process of Separation.*—In bringing the above subject under notice, it is necessary to allude to some of the facts distinguishing this very interesting metal.

Bismuth, in some of its important characteristics and reactions, resembles lead. And one of the chief points of resemblance between these metals is their ready oxidation, and their absorption by bone-ashes or wood-ashes whilst so oxydised. I refer of course, to the process of cupellation.

This ancient and serviceable process, still employed universally for the separation of gold and silver from lead, is equally applicable to bismuth, if associated with these precious metals; and, like lead, bismuth may be readily employed as a vehicle or means of collecting gold and silver from their ores in reduction processes; but its comparative cost accounts for its non-employment in this respect.

Commercially speaking, bismuth differs from lead in its greater value, lead being worth at present £13 to £14 per ton,\* whilst bismuth realises between £700 and £800 per ton; this high value being due to its greater rarity and to its limited and special uses.

As is well known, bismuth ores are frequently auriferous; and one of the points which it is my desire to bring under notice is the effectual separation of the gold from bismuth by a rapid and efficacious process.

Of course, nothing could be easier than to separate these two metals by the ordinary process of cupellation. The gold, by these

\* June, 1886.

means, is at once rendered available, but with the drawback that not only is there a very considerable loss of bismuth by volatilisation during the cupellation, but the subsequent recovery of the metal, which in the state of oxide has been absorbed by the cupel, is rendered necessary, involving a tedious and troublesome smelting operation, the employment of expensive fluxes, and a further considerable loss of metal.

Bearing in mind the close resemblance of bismuth to lead in its behaviour in the cupellation process, I directed my attention to its separation from gold by means of the addition of a small proportion of zinc—a method known as the Parkes process, as employed for the separation of silver from lead. And this I found successful, the natural separation of these two metals during the process of cooling proving to be similar in both cases.

The operation as carried out by me is as follows :—

The Bismuth holding the gold is melted at the ordinary temperature, about two per cent. of melted zinc is then added, and the whole brought to a dull red heat. The alloy is then well stirred, and the temperature gradually lowered. When at a black heat the slight crust formed on the surface is skimmed off and the metal again treated with a further quantity of zinc at the higher temperature. *The whole of the gold* will be found in these skimmings, and the bismuth will be thus freed from it.

The skimmings, consisting of bismuth, gold and zinc, and zinc oxide, I now treat by a process which quickly renders the gold available, and at the same time has the effect of *refining* the gold from all impurities excepting silver during the actual process of extraction.

This small proportion of bismuth litharge and its charge of gold is fused in a clay crucible with a little borax, and allowed to cool down in the crucible, or it is poured into a mould with the bismuth litharge, which being perfectly liquid, allows the metallic gold to separate by its own gravity, and during its fusion absorbs any base metals associated with it as oxides. *The bismuth litharge, in fact, acts as a refining agent to the gold*, which, when cold, is detached from it. This bismuth slag is broken up, re-fused with a little metallic bismuth, and is so freed from the last trace of gold which is collected by the bismuth, and subsequently extracted. The bismuth litharge so freed from gold is then reduced by fusion with carbon to its metallic state.

The quantity of bismuth litharge holding the gold is exceedingly small in proportion to the bulk of metal originally treated, as the figures hereinafter given will show ; but, by this process the bismuth is at once freed from its gold contents with little time, labour, or expense.

I have continuously carried out this method of treatment with the

most satisfactory results. It will only be necessary to take the figures of one operation as an illustration.

A quantity of 9483 lbs. of bismuth, holding about one per cent. of impurity, and 12·5 ounces of gold per ton (equal to 53·5 ounces in the bulk), was so treated, and of this nearly 9000 lbs. was immediately rendered available for commercial use, the skimmings, which amounted to 658 lbs. (7·30 per cent. of the bulk), *containing the whole of the gold.*

These skimmings I oxidised by means of nitric acid, thus obtaining the greater proportion of the bismuth and what little copper there was in solution, from which the bismuth was precipitated by the ordinary method, care being taken to saturate the nitric acid by extracting the greater portion of the bismuth as nitrate, so as to leave a portion of the bismuth as oxide with the gold in order to refine it from the impurities existing as oxides when fused with it. This residue, collected and dried, was, when dried, fused in clay crucibles, with a small quantity of borax, yielding the full amount of gold shown by assay.

As before stated, in these fusions the metallic gold separates from the bismuth litharges, and descends to the bottom of the crucible by its own gravity. The liquid and supernatant bismuth litharge floats upon it and breaks away readily when cold, the gold so obtained being associated only with silver, both metals being in fact *refined by the action of the bismuth litharge.*

§ 2. *Separation of Bismuth from Lead.*—The difficulty surrounding the treatment of bismuth associated with other metals by any rapid or comprehensive process is well known to the metallurgical chemist. I believe I am correct in stating that hitherto the only process employed for the refining of bismuth on the Continent—notably in Saxony, the chief continental source of this metal—has been that of chlorination and subsequent precipitation, a process tedious in itself and involving much plant and labour in comparison with the quantities of metal operated upon.

Rapidity of production with a minimum margin of loss, in order to free the metal from its impurities and render it marketable as quickly as possible, being a great desideratum, induced me to turn my attention to its refining by dry processes. In carrying this out I have found present most of the metals which are easily seized by and become associated with the bismuth itself during the process of reduction from its ores,\* such as antimony, arsenic, tellurium, lead, copper, &c., &c., all of which I have successively and successfully dealt with.

It is not my intention in this paper to describe the processes adopted for the elimination of these several metals, but to confine

\* See Table of Analyses herewith.

myself to the separation of lead, the presence of which especially presented at first great difficulties.

As stated above, I have found that I can separate one by one the metals mentioned above, all of which have been associated with crude bismuth which has come under my notice. In this, success though gradual, has been complete: but I was still confronted by the fact that the lead alloy was retained by the bismuth with a most characteristic persistency which seemed to defy all efforts of separation excepting by tedious wet or acid processes.

The amount of lead existing in the bismuth I operated upon, after freeing it by dry processes from its other impurities, varied from 2 to 10 per cent.

Bearing in mind the respective fusing points of lead and bismuth, it occurred to me that, as alloys of bismuth and lead fuse at a temperature considerably lower than that of bismuth itself, separation would possibly take place between the two metals at a certain point of cooling; I therefore made the following experiment:—

Taking a quantity of bismuth (about 10 cwt.), holding 11·5 per cent. of lead, and fusing same, I allowed the metal to cool until the major part of it had crystallised, then removing the fluid portion.

The residue showed by assay only 6·35 per cent. of lead, pointing at once to the partial separation I had hoped for.

These crystals again similarly treated showed only 3·75 per cent. of lead.

The operation repeated gave crystals with only 2 per cent. of lead, and a fourth crystallisation brought this down to below 0·5 per cent.

As a matter of possible interest, I subjoin the progressive results during the crystallising operations of several lots up to the point of bulking, and of finally separating every trace of lead:—

*Bismuth holding 14·6 per cent. Lead.*

1st crystallisation gave crystals holding 9·8 per cent. of lead.						
2nd	"	"	"	5·1	"	"
3rd	"	"	"	3·8	"	"
4th	"	"	"	2·5	"	"
5th	"	"	"	0·4	"	"

*Bismuth holding 12 per cent. Lead.*

1st crystallisation gave crystals holding 6·2 per cent. of lead.						
2nd	"	"	"	4·2	"	"
3rd	"	"	"	1·4	"	"
4th	"	"	"	0·4	"	"

*Bismuth holding 7·6 per cent. Lead.*

1st crystallisation gave crystals holding 4·8 per cent. of lead.

2nd	"	"	"	3·8	"	"
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3rd	"	"	"	0·8	"	"
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4th	"	"	"	0·4	"	"
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*Bismuth holding 11 per cent. Lead.*

1st crystallisation gave crystals holding 5·5 per cent. of lead.

2nd	"	"	"	2·5	"	"
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3rd	"	"	"	1·0	"	"
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*Bismuth holding 5·6 per cent. Lead.*

1st crystallisation gave crystals holding 2·0 per cent. of lead.

2nd	"	"	"	0·7	"	"
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3rd	"	"		under 0·5	"	"
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*Bismuth holding 5·3 per cent. Lead.*

1st crystallisation gave crystals holding 1·8 per cent. of lead.

2nd	"	"	"	0·6	"	"
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3rd	"	"		under 0·5	"	"
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Having attained this point, I worked upon several large quantities of metal—with practically the same results—finally succeeding by a continuation of the process in eliminating every trace of lead.

By the above it will be seen that the process becomes an exceedingly simple one, large quantities being treated at one time, involving little or no loss, and occupying hours, instead of possibly weeks.

To illustrate the facilities of the separation of lead and bismuth alloys, I give the following figures from metal holding originally five per cent. of lead.

10,675 lbs. produced, in the course of six to seven crystallisations, 9306 lbs. of available bismuth, the residue 1188 lbs. holding 40 per cent. of lead, so that from a quantity of nearly 5 tons of bismuth and lead alloy only about half a ton remained, holding practically the whole of the lead; the bulk of the bismuth separated by simple crystallisation holding traces only of lead, which, if necessary, could be readily eliminated by further crystallisation. From these facts it is apparent that the separation of these two metals can be effected by turning to account their *relative fusing points*.

*Recapitulation of foregoing Experiment.*

10,675 lbs. leady bismuth, holding five per cent. lead, yielded 9306 lbs. of good commercial bismuth by the crystallization process, or within six per cent. of the total contents of pure bismuth.

Leaving for subsequent treatment—

Of alloy, holding 40 per cent. of lead, 1188 lbs., which is equal to 11·13 per cent. of the whole weight of metal treated.

*Average Analysis of the Bismuth Ores worked upon.*

Bismuth.....	44·57
Lead.....	2·35
Antimony.....	0·64
Arsenic.....	1·26
Molybdenum.....	5·02
Tellurium.....	0·17
Iron.....	5·25
Manganese.....	0·05
Copper.....	0·24
Tungstic acid.....	2·45
Alumina.....	0·18
Magnesia.....	0·09
Lime.....	0·81
Carbonic acid.....	1·47
Sulphur.....	3·77
Insoluble earthy matter, chiefly silica.....	23·12
Water.....	3·37
Oxygen in combination and loss.....	5·19
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- II. "An Inquiry into the Cause and Extent of a special Colour-Relation between certain exposed Lepidopterous Pupæ and the Surfaces which immediately surround them." By EDWARD B. POULTON, M.A., of Jesus and Keble Colleges, Oxford, Lecturer in Zoology and Comparative Anatomy at St. Mary's Hospital, Paddington. Communicated by Professor E. RAY LANKESTER, F.R.S. Received February 10, 1887.

(Abstract.)

*Historical.*—Mr. T. W. Wood first called attention to the colour-relation in pupæ ('Entom. Soc. Proc.,' 1867, p. xcix), adducing